AD-A225 305

OFFICE OF NAVAL RESEARCH

Contract N00014-82K-0612

Task No. NR 627-838

TECHNICAL REPORT NO. 52

Mass and Charge Transport in Electronically Conductive Polymers

by

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Prepared for publication

in

Molecular Design of Electrode Surfaces

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August 2, 1990

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UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
APPROVED FOR DISTRIBUTION,
DISTRIBUTION UNLIMITED.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
ONR TECHNICAL REPORT # 52

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Dr. Charles R. Martin
Department of Chemistry

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)
Colorado State University
Ft. Collins, CO 80523

7b. ADDRESS (City, State, and ZIP Code)
800 North Quincy Street
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL (If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Contract # N00014-82K-0612

8c. ADDRESS (City, State, and ZIP Code)
800 North Quincy Street
Arlington, VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification) Mass and Charge Transport in Electronically Conductive Polymers

12. PERSONAL AUTHOR(S) Charles R. Martin and Leon S. Van Dyke

13a. TYPE OF REPORT
Technical

13b. TIME COVERED
FROM _____ TO _____

14. DATE OF REPORT (Year, Month, Day)
(90, 08,02) Aug. 2, 1990

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Electronically conductive polymers, switching reactions.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

One of the most interesting properties of electronically conductive polymers is their ability to be reversibly switched between electronically insulating and electronically conductive states. A tremendous amount of research effort has been directed, during the last ten years, toward exploring the rates and mechanisms of these switching reactions. Because these reactions are electrochemical, in nature, electrochemical methods have been have been used in these investigations. In this review article we review both electrochemical and chemical methods for studying insulator/conductor switching processes in electronically conductive polymers.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL
Dr. Robert Nowak

22b. TELEPHONE (Include Area Code)
(202) 696-4410

22c. OFFICE SYMBOL

DD Form 1473, JUN 86 Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

ONR Tech Report #52
To be published in "Molecular Design of Electrode Surfaces," R. W. Murray, Ed.

Mass and Charge Transport in Electronically Conductive Polymers

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I. INTRODUCTION

Electronically conductive polymers are an exciting new class of materials with unique electronic, electrochemical, and optical properties. Because of these unusual and useful properties, electronically conductive polymers are the focus of a massive international research effort. The players in this research effort include physicists, physical chemists, materials scientists, synthetic organic chemists, engineers, and electrochemists. Indeed, in the preface of his recent monograph on conductive polymers, Skotheim states that "this is unarguably one of the most interdisciplinary fields of science today" (1). As a result of this large and interdisciplinary research effort, the scientific literature of conductive polymers is massive and diverse. Fortunately, a number of informative review articles and monographs have recently appeared (1-6).

One of the most interesting and potentially useful aspects of these polymers is that they can be reversibly "switched" between electronically insulating and electronically conductive states. This switching reaction involves either oxidation or reduction of a non-ionic and electronically insulating parent polymer to form a conductive polycationic or polyanionic daughter polymer. The electrochemical oxidation process might be represented by

$$-[M]_y- \;+\; nX_s^- \;\text{-------->}\; -[M^+X^-]_n-[M_{(y-n)}]- \;+\; ne^- \qquad (1)$$

where M represents a monomer unit in the nonconductive form, M^+ is the corresponding oxidized unit in the conductive form, and X^- is an anion initially present in a contacting solution phase. Equation 1 shows that the

electrochemical switching reaction involves a charge-transport process in which oxidized monomer sites and charge compensating counterions diffuse through the polymer film.

The oxidative switching reaction shown in Equation 1 could also be accomplished using a chemical oxidizing agent, Ox.

$$-[M]_y- + nOx \text{ -------->} -[M^+Ox^-]_n-[M_{(y-n)}]- \qquad (2)$$

Equation 2 shows that the chemical switching reaction also incorporates a diffuse component but, in this case, it is the chemical oxidant which diffuses through the film.

The oxidation/reduction reactions (Equations 1 and 2) play an integral role in nearly all of the proposed technological applications of electronically conductive polymers. For example, one of the most widely publicized applications of these polymers is as electrode materials in secondary batteries (7). In this case, the forward direction in Equation 1 would correspond to the charge reaction and the reverse direction in Equation 1 the discharge reaction for the battery. Other proposed applications include use as electrochromic devices (8), where the reaction in Equation 1 is responsible for the color change, and as transistors (9), where this reaction is responsible for turning the device on and off.

The rates of these redox reactions are of particular importance to the proposed technological applications of conductive polymers. For example, the rate of the redox reaction will determine the current density achieved by a conductive polymer battery and will determine the switching rate of a polymer-based electrochromic or electronic device. Therefore one of the primary

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objectives of the conductive polymer research effort has been to quantitatively evaluate the rates of oxidation and reduction of these polymers.

In spite of the importance of the redox rate, there has, as far as we know, been no comprehensive review of this particular aspect of electronically conductive polymer research. The objectives of this manuscript are to provide a critical review of the methods used to investigate the rates of redox reactions of electronically conductive polymers and to assess the current status of this important aspect of conductive polymer research. As we shall see, both chemical and electrochemical methods have been used to investigate redox reaction rates in these polymers; both of these classes of methods will be reviewed here.

This manuscript is organized as follows: First, we briefly review the synthesis of electronically conductive polymers. Synthesis is important because the synthetic procedure often determines the methods used to evaluate the redox reaction rate. We then present a critical review of <u>electrochemical</u> methods for evaluating the redox reaction rates of electrochemically conductive polymers. We expose methods which are unreliable or produce questionable results and identify procedure which should yield meaningful rate data.

Following the section on the electrochemically techniques, we discuss <u>chemical</u> methods for assessing redox rates in electronically conductive polymers. This section includes methods which follow the doping and undoping of the polymer and also methods which measure diffusion coefficients at fixed polymer redox potentials. Again, we attempt to identify the methods which will yield reliable results.

We then give our assessment of what is currently known and what remains to be learned about the rates of redox reactions in conductive polymers. This section also discusses various ancillary methods which do not directly provide the redox rate but yield information which is relevant to determination of the redox rate. In the final section of this paper we discuss methods for enhancing the rates of oxidation and reduction of electronically conductive polymers.

II. SYNTHESIS OF ELECTRONICALLY CONDUCTIVE POLYMERS.

Electronically conductive polymers can be synthesized either electrochemically or chemically. Synthesis is an important issue because, from a historical perspective, chemical methods for evaluation of redox rates have been used for chemically synthesized electronically conductive polymers; in contrast, electrochemical methods have been used almost exclusively for the electrochemically synthesized polymers.

The most common electrochemically synthesized conductive polymers include polypyrrole and its analogues, polythiophene and its analogues, and polyaniline (10,11). These polymers are usually synthesized from a solution of the corresponding monomer via electropolymerization (10); the polymer typically precipitates as a thin film onto the electrode surface. Because the synthetic procedure yields a polymer film-coated electrode, these polymers are ideally suited for subsequent investigations using electrochemical methods.

Polyacetylene is the most common chemically synthesized electronically conductive polymer. Polyacetylene is also the first and prototypical organic conductive polymer. Polyacetylene is usually synthesized via the direct polymerization of acetylene over a Ziegler catalyst (12). When synthesized at

room temperature, a mixture of both cis and trans-polyacetylene is formed (12). The polymer can be converted to the all trans-form (the thermodynamically stable form) by heating at 200° C.

Electron microscopy shows that polyacetylene has a fibrous morphology. As a result, the bulk density of polyacetylene film is ca. 0.4 g cm^{-3} whereas the density obtained by flotation techniques is ca. 1.2 g cm^{-3} (13). Thus, the polymer fibrils (fibrils are small fibers) fill only about 33 percent of the total film volume. As we shall see, this fibrous morphology greatly complicates evaluations of rates of oxidation or reduction of this polymer. Because polyacetylene is synthesized chemically, the majority of the redox rate data in the literature, for this polymer, have been generated using chemical methods.

Polyacetylene can also be synthesized via the so called "Durham" method: this methods involves the synthesis of a precursor polymer which, when heated, undergoes elimination to yield polyacetylene (14). In contrast to polyacetylene synthesized via the conventional Shirakawa technique (15), the Durham route yields a dense, amorphous, nonfibrous form of the polymer. The transport properties of the Durham and Shirakawa polyacetylenes are quite different (16).

Finally, it is worth noting that polypyrrole, polythiophene, polyaniline and others of the electrochemically synthesized polymers can also be synthesized chemically (11,17). The chemical synthesis entails replacing the electrode with a chemical oxidizing agent. However, the quality of the polymer film obtained via this approach is usually so poor that electrochemical syntheses of these polymers are much more popular.

III. ELECTROCHEMICAL METHODS FOR EVALUATING THE RATES OF REDOX REACTIONS.

As noted above, the electrochemically synthesized electronically conductive polymers usually precipitate as thin films which coat the electrode surface. Thus, the electrosynthesis produces a "polymer-modified electrode" (18,19), a fact which has had tremendous (and unfortunate) impact on the way in which redox reaction rates for these polymers have been investigated.

Polymer-modified electrodes have, during the last decade, been of considerable interest to electrochemists (18,19). Most of the research effort in this area has focused on redox polymers (18,19); these polymers contain electroactive groups and can transport charge via electron self-exchange between these groups (18,19). The relevance of this work to electronically conductive polymers is twofold. First, the self-exchange events are initiated by using the substrate electrode to oxidize or reduce the polymer; the net reaction is identical to the reaction shown in Equation 1. Second, a number of relatively simple electrochemical methods have been devised to evaluate the rate of oxidation and reduction of redox polymers (19-24).

Large amplitude potential-step experiments are the most commonly used class of methods for evaluating the redox reaction rates of redox polymers (19-24). These methods treat the redox reaction as a diffusion of electrons or holes from site the site through the film (19-24). This diffusion process is assumed to be linear to, or from, the substrate electrode surface. The rate of this diffusional charge-transport process is expressed in terms of an "apparent diffusion coefficient", D_{app}. D_{app}'s associated with redox reactions in redox polymers have varied from as low as ca. 10^{-13} cm^2 s^{-1} (25) to as high as 10^{-5} cm^2 s^{-1} (26).

Because large amplitude electrochemical methods proved useful for

evaluations of oxidation/reduction rates in redox polymers, it seemed obvious that these methods could be applied to electronically conductive polymers (27-42). For example, large amplitude potential-step experiments have been used to obtain D_{app}'s (or a derivative thereof) for polypyrrole (27-29), for substituted polypyrroles (30-32), for polythiophene (33), for poly(3-methylthiophene) (34), for polyaniline (35-37), for composites of polypyrrole with other polymers (38-40), and for various other conductive polymers (41,42). Indeed, these large amplitude methods have provided the majority of the experimental redox-rate data available in the literature to date.

It is now well established (although perhaps less well known) that the D_{app}'s obtained from large amplitude potential-step experiments at conductive polymer film-coated electrodes are essentially meaningless (43,44). Since this is a rather brazen statement, the corroborating evidence, both theoretical and experimental is reviewed in the following paragraphs. We then discuss electrochemical methods which, in our opinion, do yield reliable D_{app}'s for electronically conductive polymers.

Fritz Will was the first to point out a major problem associated with electrochemical (and chemical) determinations of apparent diffusion coefficients in electronically conductive polymers (45-47). With regard to electrochemical methods, this problem can be stated in terms of a question - what is the active electrode area (45-47)? This is an important question because, nearly all electrochemical methods for determination of D_{app} are dependent on an accurate value for the electrode area (48).

Most researchers who use large amplitude methods to evaluate D_{app}'s for conductive polymers assume that the active electrode area is just the area of the substrate electrode (27-42). However, because the conductive state of the

polymer resembles a porous metal (49,50), this simplifying assumption is clearly not valid (43). Thus, as pointed out by Will, the active electrode area is, in most cases, unknown and accurate determinations of D_{app} are impossible (45-47).

Murray et al. pointed out a second problem associated with the application of conventional electrochemical methods to the determination of apparent diffusion coefficients in electronically conductive polymers (51). The total current in an electrochemical experiment is composed of the faradaic current and the capacitive (double layer charging) current. The faradaic component must be isolated from the total current if D_{app} is to be determined. Unfortunately, because these polymers behave like porous electrodes, the capacitive-like (49,50) component of the current often overwhelms the faradaic component (50,51).

The magnitude of the capacitive-like (49,50) current would not be a problem if a reliable means for discriminating against or subtracting this component could be devised. We have pointed out, however, that when a large amplitude perturbation is applied to a conductive polymer, it is usually impossible to separate out the capacitive component (43). For example, assume that the initial potential in a potential-step experiment is such that the polymer is in its nonconductive form. The final potential will then be to the region where the polymer is in its conductive from. Thus, the polymer is converted from an insulator to a conductor during the course of the experiment.

Because the polymer is converted from an insulator to a conductor, at some time during the experiment, a large capacitive-like current must flow to charge the double layer of the newly created "porous metal-like" film (50).

However, the time course of delivery of this capacitive-like current is unknown. Therefore, the traditional methods based on temporal discrimination (48,52) against the capacitive component will not work with conductive polymers (43).

We have identified several other problems associated with the use of large amplitude methods for determination of D_{app}'s in conductive polymers (43). First, these methods usually assume that the rate of the redox reaction is diffusion-controlled, yet the experimental data (vide infra) suggest otherwise. Second, as noted above, these methods assume that diffusion is linear to the substrate electrode; however, when the film is in its conductive state, there is no reason to assume that linear diffusion is obtained (44,53).

Finally, there is the "apples-to-oranges" problem (43,51). The reduced form of the conductive polymer is usually a non-ionic, hydrophobic, insulating organic polymer. In contrast, the oxidized form is usually a polycationic, hydrophilic, electronically conductive polymer. These are very different materials, and it would be highly unlikely that they would show the same charge and mass-transport characteristics. Nevertheless, a large amplitude method converts one form into the other during the course of the experiment (i.e. converts an apple to an orange) and attempts to ascribe a single rate parameter (D_{app}) to these very different materials.

We have presented a variety of arguments which suggest that large amplitude methods can not be used to obtain reliable and meaningful apparent diffusion coefficients for redox reactions in electronically conductive polymers. These arguments would, however, be specious if the experimental data in the literature conformed to the predictions of the relevant theoretical model. In fact, the experimental data are almost always at odds

with results predicted by the relevant electrochemical model.

For example, Genies et al. show "Anson plots" (28) associated with chronocoulometric experiments at polypyrrole film-coated electrodes (28). If the rate of the polymer redox reaction is diffusion-controlled, these plots should be linear with zero or positive intercepts (52). In fact, the experimental plots have negative intercepts (28). Furthermore, the slopes of these plots (and therefore the value of D_{app} obtained) increased with the positive limit of the applied potential-step (28). The negative intercept and the potential dependent slope observed by Genies et al. (28) suggest that the charge-transport reaction is activation rather than diffusion controlled (52).

Kaneto et al. conducted analogous experiments on polythiophene (33). They, again, observed potential dependent D_{app}'s, something that should not happen if the redox reaction is diffusion-controlled. Kaneto et al. suggest that either migration or activation effects cause the D_{app}'s to vary with potential (33). The fact that polypyrrole and polythiophene contain large concentrations of electrolyte suggests that migration should not be a problem for these films (43,54). Pickup and Osteryoung have conclusively shown that migration occurs in the oxidized form of the polymer (44,53). In any event, it is difficult to ascribe a physical meaning to D_{app}'s which, in direct contradiction to theory, are potential dependent.

Reynolds et al. have recently reported some interesting results from potential-step experiments on polypyrrole and a sulfonated derivative of polypyrrole (32). Instead of plotting chronocoulometric data in the conventional fashion (charge (Q) vs. $t^{1/2}$), Reynolds et al. plotted these data as logQ vs. logt; these plots were roughly linear but the slopes were rarely the theoretically predicted 0.5. Indeed, the slopes of the log-log plots were

both potential and ion-dependent (32). These data, again, provide compelling evidence that a simple linear diffusion model is not applicable when large amplitude potential-steps are applied to conductive polymers.

So far we have discussed methods that will not yield meaningful data for redox rates for conductive polymers. As indicated above, we chose to discuss these methods first because they are the most commonly used methods. The question now becomes - what methods will yield reliable redox rate data for conductive polymers?

It might first be useful to discuss, in general terms, the characteristics that a method for evaluating redox rates of conductive polymers should possess. In our opinion, the first prerequisite is that the method involve a small amplitude electrochemical perturbation (43). As noted above, large amplitude methods by nature convert the polymer from an insulator to a conductor and these are very different materials. Thus, we believe that small amplitude methods, which cause only minor perturbations in polymer structure and which avoid the potential region where the polymer is switched, should be employed.

The second prerequisite is that a reliable theoretical model which accurately reflects the nature of the transport process and which accounts for or obviates the effects of slow heterogeneous electron transfer must be available. With regard to transport, if the polymer is in its reduced form, a linear diffusion model is probably appropriate (see below and (43)). However, if the polymer is in its conductive state an alternative model will usually be required (44,53).

Finally, the ideal method for evaluating the rates of redox reactions for conductive polymers would be easy to use and would be applicable to a

variety of polymers. The latter point is important in that, as it stands now, it is difficult to make meaningful comparisons of redox rates for different conductive polymers. These data are essential if the best polymer for a particular technological application is to be identified.

Fritz Will described a current-pulse method which satisfies most of these conditions (45-47). This current-pulse method was applied to polyacetylene and was initiated in a potential region where the polyacetylene was in its conductive state. The polymer remained in the conductive state throughout the duration of the experiment (45-47). It is of interest to note, however, that this method is based on a linear diffusion model. This model worked for the conductive form of polyacetylene because Will chose a solvent which did not solvate the polymer (45-47). As a result, only the external surface of the polymer was wetted and thus diffusion was linear to or from this surface (45-47).

The above discussion indicates that Will's method (which is based on pioneering work by Paul Delahay (55)) solves the electrode area, diffusion model, and apples-to-oranges problems. In addition, the rate of the diffusive component of the redox reaction (as described by D_{app}) can be separated from the rate of heterogeneous electron transfer (as described by the exchange current density, I^{o}). Indeed, Will was the first to present reliable kinetic data for redox reactions of electronically conductive polymers (45-47).

Unfortunately, it seems to us that it is difficult to apply Will's method to most electronically conductive polymers. For example, if the conductive form of a polymer is to be analyzed (as was the case in Will's analysis of polyacetylene) a solvent which does not solvate the polymer must be identified. Conventional electrochemical solvents (e.g., acetonitrile,

water, N, N'-dimethylformamide, etc.) solvate most conductive polymers quite strongly. Thus, a more exotic solvent must be used.

Furthermore, it seems unlikely that Will's method could be applied to the reduced (i.e. insulating) form of a conductive polymer because relatively large quantities of charge are injected into the polymer during this current-step experiment. Because it usually takes only minute quantities of charge to convert the reduced form of the polymer to an electronic conductor (56,57), it seems likely that, if Will's method was applied to the reduced form, the apples-to-oranges (vida supra) problem would be encountered. Furthermore, while diffusion would be linear to the substrate electrode when the polymer is an insulator (very short times), diffusion would not be linear when the polymer is converted to a conductor (long times).

What reliable yet widely applicable methods are available for evaluating D_{app}'s for electronically conductive polymers? In our opinion, the best methods currently available are AC impedance methods (58-61). These are inherently low amplitude methods so that only minor perturbations of the polymer are required (58-61). Reasonable theoretical models are available which allow for relatively straight forward evaluation of D_{app} (62). Furthermore, the effects of heterogeneous electron transfer can be isolated from the diffusive component of the charge-transport process and both heterogeneous kinetic and D_{app} data can be obtained (63). Finally, in addition to D_{app} and kinetic data, a wealth of information about both the insulating and conducting forms of these polymers can be obtained from AC impedance methods (49,61,64-66).

Perhaps the most negative comment which can be made about the AC impedance methods is that they assume that the electrical response of the

conducting polymer film-coated electrode is identical to that of a particular electrical circuit (the "equivalent circuit"). The reliability of the data obtained is determined by the degree to which the electrical response of the polymer system actually agrees with that of the equivalent circuit. While reasonable agreement has been observed in AC-based D_{app} determinations, some discrepancies have been noted (58,59).

We have used an AC impedance method to evaluate D_{app}'s for the reduced form of polypyrrole (58). Rubinstein et al. have conducted analogous experiments on polyaniline (59). Jow and Shacklette have used an analogous AC impedance method to determine D_{app}'s in polyacetylene (60). In addition AC-impedance methods have made significant contributions toward an understanding of the fundamental electrochemical properties of electronically conductive polymers (49,58-66).

In addition to the AC impedance methods, we have recently described a low amplitude current-pulse method for determination of D_{app}'s for electronically conductive polymers (43). Again, the low amplitude character of this method is important; the experiment is initiated with the polymer in the reduced (non-conductive) state and the polymer remains in this state throughout the duration of the experiment. Because the polymer is nonconductive, a finite linear diffusion model, based on heat transfer in a slab of finite thickness (67), is applicable (43). D_{app}'s are obtained by matching experimental and simulated E vs. time transients (43).

The down side of this new current pulse-method is that it is experimentally tedious and time consuming. The tedium arises because of the need to experimentally define the relationship between the open circuit potential and the extent of oxidation of the polymer and because background

capacitive contributions must be evaluated. Because of these experimental difficulties we believe that the AC impedance experiment (58-60) is currently the method of choice.

The above methods are valid for determining the diffusion coefficients in the neutral insulating form of electronically conductive polymers. However, as we have pointed out earlier, the conductive form of the polymer is a very different material and therefore a different model for the determination of diffusion coefficients will be necessary.

Osteryoung and Pickup have developed such a model, which treats the polymer film as a porous electrode (44,53). Potential step chronoamperometry was used to investigate charge-transport in polypyrrole. However, instead of modelling the data by traditional Cottrell theory (48), which we have already shown will not work, they use a porous electrode model based on the pioneering work of Posey and Morozumi (68). In this model all of the charge is assumed to be capacitive and all of the current is carried by migration. This allows the polymer to be characterized in terms of a film ionic resistance and capacitance. If one knows (assumes) the number of ionic sites in the polymer a diffusion coefficient can be calculated from the ionic film resistance (44,69).

It should be pointed out that this model only works if the polymer remains in its oxidized conductive state during the entire experiment (ie. the potential is stepped from a potential where the polymer is oxidized to a second potential where the polymer remains oxidized). Thus this too meets our requirement of being a small amplitude technique. If a large amplitude potential step is used such that the polymer is switched from its oxidized form to its reduced form the capacitive model does not accurately fit the

data. Thus, this model does not allow accurate determination of the switching rate for electronically conductive polymer. However, since a considerable amount of the charge which these polymers store is capacitive in nature, the porous electrode model should prove very valuable. It also allows for calculation of ionic diffusion coefficients for the oxidized form of the polymer (44).

One disadvantage of the chronoamperometric technique is that it requires the independent determination of uncompensated solution resistance. We have recently developed a small amplitude current step experiment (70) in which the data is treated using the porous electrode model of Posey and Morozumi (68). The polymer is again characterized in terms of capacitance and ionic film resistance. One advantage of this technique over the chronoamperometric technique is that it does not require the independent determination of uncompensated solution resistance. We have used this technique to study thin polypyrrole films in their oxidized conductive state. The porous electrode model fits the data extremely well when the polymer remains in its oxidized state (70).

IV. CHEMICAL METHODS FOR EVALUATION OF THE RATES OF REDOX REACTIONS OF CONDUCTIVE POLYMERS.

The chemical methods for evaluating the rates of redox reactions in conductive polymers are based on following the rate of the chemical "doping" reaction shown in Equation 2. These methods have been used almost exclusively with polyacetylene which, as noted earlier, is a chemically synthesized conductive polymer. Chien, in his definitive text on polyacetylene, reviews some of the early attempts to evaluate the rate of the doping reaction in this

polymer (71). These methods usually involved investigations of the rates of diffusion of oxidants such as I_2 into polyacetylene films (72-75).

As discussed in detail by Chien (71), polyacetylene's fibrillar morphology complicates analyses of these diffusion data. Because of this morphology, two diffusional processes must be considered, the relatively fast diffusion of the dopant into the interfibrillar space and the slower diffusion of the dopant into the fiber itself. Furthermore, the interfiber diffusion is complicated by the fact that diffusion is accompanied by chemical reaction of the dopant with the polymer chain and by the crystallinity present within the polymer fibers (71).

Because of these complications, Chien maintains that diffusion of dopant into polyacetylene can never be analyzed in terms of a single Fickian process (71). More importantly, Chien states that "one must come to the conclusion that determination of the diffusion constant for the chemical doping of polyacetylene is a futile exercise. The results are almost always without significance."

Many groups have studied the chemical doping polyacetylene since Chien's review (76-81). Some recent studies have taken into account the morphological complications pointed out by Chien (80,81). The chemical doping of Durham polyacetylene which does not involve the morphological complications of Shirakawa polyacetylene has also been studied (16). However, the authors found that diffusion was complicated by both dopant reactions with the polymer and the physical properties of the polymer including morphology, dopant/solvent swelling, and crystallinity (16). Furthermore, the diffusion coefficients measured for initial doping, undoping, and redoping often vary widely (16). We believe therefore that Chien's conclusions are essentially

correct. Furthermore, Scrosatti has analyzed some of the models used for chemical doping studies and has shown them to be based on invalid assumptions (82).

We believe therefore that a new model is necessary for the proper interpretation of chemical doping of conducting polymers. Reiss and coworkers have recently developed such a model for the gas phase iodine doping of polythiophene (83). The model is based on thermodynamically reversible trapping of the dopant and can account for the disparity in the time required to dope and undope conductive polymers using gas phase dopants.

Reiss et al. found that the gas phase iodine doping of polythiophene is thermodynically reversible. They show that the disparity in diffusion rates between doping and undoping can be explained by a reversible trapping of the diffusants. In this model an individual dopant molecule in the polymer can be considered to be either "free" or "trapped". The effective diffusion coefficient D_e, for the doping process will be equal to the diffusion coefficient of the free dopant D (the maximal value) when the concentration of free dopant greatly exceeds the equilibrium constant for trapping α. However if α is much greater than the concentration of free dopant, then $D_e = \alpha D$ (the minimal value).

During the doping process, the concentration of free dopant is high and therefore $D_e = D$. However during the undoping process the concentration of free dopant at the polymer surface is low producing a region at the polymer surface where $D_e = \alpha D$. This region at the film surface, where the diffusion is low, limits the rate of the undoping process which is often orders of magnitude slower than the doping process. This model has recently been improved and confirmed by a more rigorous theoretical treatment (84). This

type of theoretical model is an important step toward developing a better understanding of the doping/undoping process in electronically conductive polymers. Reiss's extremely important work deserves an additional comment. It is of interest to note that the peak current for the reduction of (e.g.) polypyrrole is always lower than the peak current for the oxidation of the polymer. This may result from trapping as described by Reiss et al. (83,84).

The chemical methods for the determination of diffusion coefficients discussed above rely on the diffusing species to "dope" the electronically conductive polymer. As indicated earlier this complicates the situation because the dopant both diffuses and reacts. Several methods have been developed in which the oxidation state of the polymer is held constant; thus, the reaction step is eliminated. These methods are discussed below.

The first one of these methods is based on ion self-exchange. Schlenoff and Chien have used this method to measure diffusion coefficients in p-doped polyacetylene and polypyrrole (85). For both polymers, the ion self-exchange kinetics can be modelled using finite, planar Fickian diffusion. As noted earlier, however, electronically conducting polymer films often consist of two phases: the polymer and solvent filled pores. For Fickian diffusion to hold, the polymer/solvent system must act as an "effective medium". That is to say, the diffusing ionic species must make an infinite number of transitions between the polymer phase and the solvent phase during the course of the experiment. Thus, the measured diffusion coefficient is a combination of slow diffusion through the polymer phase and rapid diffusion through the solution phase. Schlenoff and Chien showed that the effective medium model is applicable for polypyrrole and polyacetylene (85).

Anion exchange in polypyrrole was also studied by Reynolds and co-

workers (86). Polypyrrole was electropolymerized in an acetonitrile solution containing the tosylate anion. The polypyrrole film was exposed to aqueous solutions containing various electrolytes. The leaching out (anion exchange) of the tosylate anion into the contacting solution was measured spectrophotometrically. The data were treated using a model similar to Schlenoff and Chien's. In general, the diffusion coefficients measured by Reynolds (86) were about 3 orders of magnitude lower than those measured by the self-exchange method of Schlenoff and Chien (85). This may be due to the different polymerization conditions and ions used in the two experiments (85,86).

Another chemical method for the determination of diffusion in electronically conductive polymers was developed by Burgmayer and Murray (51,68). They studied the ionic permeability of polypyrrole as a function of the oxidation state of the polymer (51,68). In this method a polypyrrole film was electrochemically deposited until it completely filled the holes of a gold minigrid electrode. This polypyrrole film was used as a separator membrane in a two compartment cell. The fluxes of various ions across the membrane were determined by monitoring their solution concentrations (51). This experiment allowed for an assessment of the effect of polymer oxidation state on the rate of ion-transport.

V. WHERE THE FIELD STANDS NOW AND RECOMMENDATIONS FOR FUTURE RESEARCH.

Most of the quantitative evaluations of the redox rates of the electrochemically synthesized electronically conductive polymers were made using large amplitude electrochemical methods (27-42); this is unfortunate because, as discussed in detail in the preceding section, it is not clear that

these data have any real significance. However, previous investigations have illuminated a number of interesting features about the redox reactions of electronically conductive polymers; we review some of these features and make recommendations about directions of future research in the following paragraphs.

First, it has been clear from the very beginning that ion-transport plays a significant role in determining the rate of redox reactions in electronically conductive polymers (87,88). Unfortunately, the ion-transport issue is not as simple as the reaction shown in Equation 1 would suggest. We and others have shown that the reduced form of polypyrrole contains large concentrations of supporting electrolyte (43,54). Therefore, when the polymer is oxidized, charge compensation can occur either by incorporation of an anion, expulsion of a cation, or both. We now discuss two techniques which can be used to resolve this issue.

The first technique is a radiotracer method in which the adsorption of radiolabeled ions into the polymer film is monitored as a function of oxidation state of the polymer (89,90). Horyani and Inzelt have used this technique to study the adsorption of labeled SO_4^{2-} and Cl^- as a function of potential for a polypyrrole coated electrode (89). Their results suggest that there is an excess of supporting electrolyte in both the oxidized and reduced forms of the polymer. They also found that approximately only 1 electrolyte anion was incorporated for every 4 electrons removed from the film. This suggests that cation as well as anion movement is important in maintaining charge neutrality in conductive polymer films (89). Similar results were found for polyaniline (90).

A second, very powerful technique which has been used to clarify the

"anion in vs. cation out" issue, is the quartz crystal microbalance (QCM) technique (91-93). Kaufman et al were the first to apply the QCM to the study of electronically conductive polymers (91). They studied polypyrrole films in propylene carbonate containing $LiClO_4$ electrolyte. They found that both Li^+ and ClO_4^- played a significant role in the charge transport process (91).

Orata and Buttry used the QCM to study ion transport in polyaniline (92). They found that the charge was carried almost exclusively by the anion. Reynolds et al used the QCM to study a sulfonated derivative of polypyrrole (93). They found that the charge was carried almost exclusively by the cations. This is to be expected since the film contained a high number of permanent anionic sulfonate sites.

In addition to studying ion transport, the QCM has been used to study the polymerization of polyaniline (92) and polypyrrole (94). Other electrogravimetric techniques have also been used to study the ion transport (95,96) and surface wetting (97) of electronically conductive polymers. Indeed, electrogravimetric techniques seem uniquely qualified for determining which of the ions of the electrolyte is the charge carrying species during redox reactions in electronically conductive polymers. Thus, a carefully planned study involving the use of the QCM to determine which ion is moving and a reliable method for evaluation of D_{app} (e.g. AC impedance) to determine the rate of diffusion for this ion would quantitatively define the role of the electrolyte in the charge-transport process.

The study suggested above would involve a number of electrolytes so that the conditions under which cation vs. anion-transport predominates could be evaluated. It is well known, however, that the morphology of a conductive polymer film is dependent on the salt used during the synthesis of the polymer

(10). Therefore, the best approach for investigating ion effects on transport might be to synthesize all polymers in a common salt and then use an ion exchange technique to convert the polymer to the desired salt-form (98). These electrolyte-induced morphology changes are, however, interesting and should be further explored (10).

A second question that needs to be answered before accurate models for charge-transport in electronically conductive polymers can developed is " What is the geometry of the redox process?". That is does the oxidation/reduction proceed from the electrode/polymer interface, the polymer/electrolyte interface, or occur uniformly throughout the polymer. Murray has previously discussed some of the factors which might affect this geometry (51). Knowledge of the geometry of this process is important for accurate modeling of diffusional processes in these films. Ellipsometry has shown that the oxidation of polyaniline occurs uniformly throughout the polymer film (57,99). Further ellipsometric studies are necessary to better understand the geometry of both the oxidation and reduction processes.

VI. ENHANCING TRANSPORT IN ELECTRONICALLY CONDUCTIVE POLYMERS

As mentioned earlier, the final section of this chapter will deal with enhancing ion transport in electronically conductive polymers. In this section we will discuss composites of electronically conductive polymers with anionic polyelectrolytes, "self-doped" conducting polymers, the use of molten salt electrolytes, and optimization of the supermolecular structure of conductive polymers for charge-transport.

One of the earliest attempts to enhance ion transport in electronically conductive polymers was to form composites of electronically conductive

polymers with anionic polyelectrolytes (38,39,100-107). The anionic sites of the polyelectrolyte act as the charge balancing counterions for the positively charged electronically conductive polymer (Equation 1). However, in contrast with small anions which are mobile, the anionic sites on the polyelectrolyte are immobilized within the polymer composite; this forces charge within the composite to be carried by cations during the oxidation and reduction of the electronically conductive polymer (38,39). Unfortunately, all attempts to measure the effect of changing from anion transport to cation transport have been made by unreliable large amplitude techniques (38,39).

The concentrations of the electronically conductive polymer and anionic polyelectrolytes within the composite can be varied to produce anion or cation exchangers (104). These composites have also found use as water deionizers (105) and as electrodes in unique polymer batteries (106). Furthermore these composites have superior mechanical properties when compared with electronically conductive polymers traditional dopants (38,39,100-107).

A second modification of ion transport in electronically conductive polymers was the synthesis of the "self-doped" polymers (107). While the term "self-doped" is a misnomer, these polymers are interesting because the covalently-attached anionic groups apparently insure that charge is carried exclusively by cations during both oxidation and reduction of the polymer (32). Furthermore, if the size of the cation is small, the rate of charge-transport is enhanced (108). Further quantitative evaluations of charge-transport rates in these interesting polymers are in order.

Another interesting electronically conductive polymer containing fixed ionic sites was recently synthesized by Pickup (109,110). As opposed to the "self-doped" polymers described above this polymer has a high concentration of

positively charged quaternary ammonium sites. In water, the reduced form of this polymer has ionic permeabilities a thousand times greater than reduced polypyrrole (109).

Ion transport in electronically conductive polymers is enhanced by the use of molten salt electrolytes (111-114). Osteryoung and coworkers have investigated the electrochemistry of electronically conductive polymers in a room temperature molten salt (111-114). The salt is a mixture of aluminum chloride and 1-methyl-3ethyl imidazolium chloride. Because of the high ionic strength of the molten salt, charge transport is much faster than in conventional aqueous and nonaqueous solvents. These media may be useful in electronically conductive polymer batteries.

Finally, ion transport in electronically conductive polymers can be enhanced by controlling the supermolecular structure of the polymer. Osaka and coworkers have developed a method for producing highly porous polypyrrole films which have higher transport-rates than conventional polypyrrole films (115-117). This method is based on coating an electrode surface with an insulating nitrile butadiene rubber (NBR). The electrolyte for polymerization ($LiClO_4$ in acetonitrile) etches channels through the NBR; pyrrole is then polymerized in these channels. After polymerization the NBR is extracted away with methyl ethyl ketone to leave a free standing highly porous polypyrrole film. Polypyrrole films produced in this manner show clearly enhanced charge transport characteristics when compared to conventional polypyrrole films. It was shown that these films had superior performance in lithium/polypyrrole batteries (115). The batteries prepared via this process had a higher charge capacity and supported a higher current density than batteries prepared in the conventional manner.

We believe that the ideal polymer supermolecular structure for fast charge-transport is one in which small diameter polymer fibrils are surrounded by solution filled pores. Polymer films with this supermolecular structure have several advantages over conventional polymer films. First, the solution filled pores become fast ion conducting channels into the film. Secondly, while counterions ultimately must enter or exit the polymer phase (Equation 1), these ions only have to traverse the narrow radius of the fiber. Finally, transport into the polymer phase is changed from a linear diffusion process, in conventional polymer films, to a cylindrical process for the fibrillar film.

We have developed a procedure for producing conductive polymers with this ideal fibrillar supermolecular structure (118-121). This procedure involves synthesis of the polymer into a host membrane which has linear cylindrical pores; these pores serve as templates for the nascent polymer. After the polymerization is completed, the host membrane is extracted away leaving isolated polymer fibers.

Figure 1 shows an SEM of polypyrrole fibers prepared by this method (121,122). It should be noted that the density of polypyrrole fibers is very high. A high density of fibers is desirable for practical applications of conductive polymers (e.g. batteries), where it is desirable to have a maximum amount of polymer in a minimal amount of volume.

A large amplitude potential step method was used compare the rates of reduction of the fibrillar and conventional polypyrrole films. In this method the polypyrrole film was first equilibrated a potential where the film was quantitatively oxidized; then the film was stepped to a potential where the film is quantitatively reduced. The charge time transient associated with the

reduction of the polymer film was recorded. Because the reduction of the film is driven to completion, the charge-time transient ultimately reaches a plateau value (e.g. Figure 2). The time required to achieve 95% of this plateau charge (t_{95}) was used as the qualitative measure of the rate of the reduction process. Comparisons of t_{95} values will be valid only if the films contain the same amount of polymer (121,122).

Figure 2 shows the charge-time transients for a conventional polypyrrole film, and a fibrillar polypyrrole film which contains the same amount of polymer. The rate of reduction for the fibrillar film is significantly higher than for the conventional film (Figure 2). This point is reinforced by the t_{95} data shown in Table I. These data clearly indicate that the rate of reductive charge-transport is faster in the fibrillar films than in the conventional films. It is also worth noting that in addition to having higher charge-transport rates, we have recently shown that extremely narrow conductive polymer fibers have much higher electronic conductivities than the corresponding conventional polymer films (122).

VII. CONCLUSIONS

The journal Science recently published an article entitled "Conductive Polymers Recharged" (123). This article discusses the many potential applications of conductive polymers and indicates that commercialization of conductive polymers has been achieved. The prospect for additional commercial applications combined with the inherently fascinating properties of these materials insures that conductive polymers will be an important research field in the twenty first century.

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Figure Captions

Figure 1 Scanning electron micrograph of 0.2 μm diameter polypyrrole fibers.

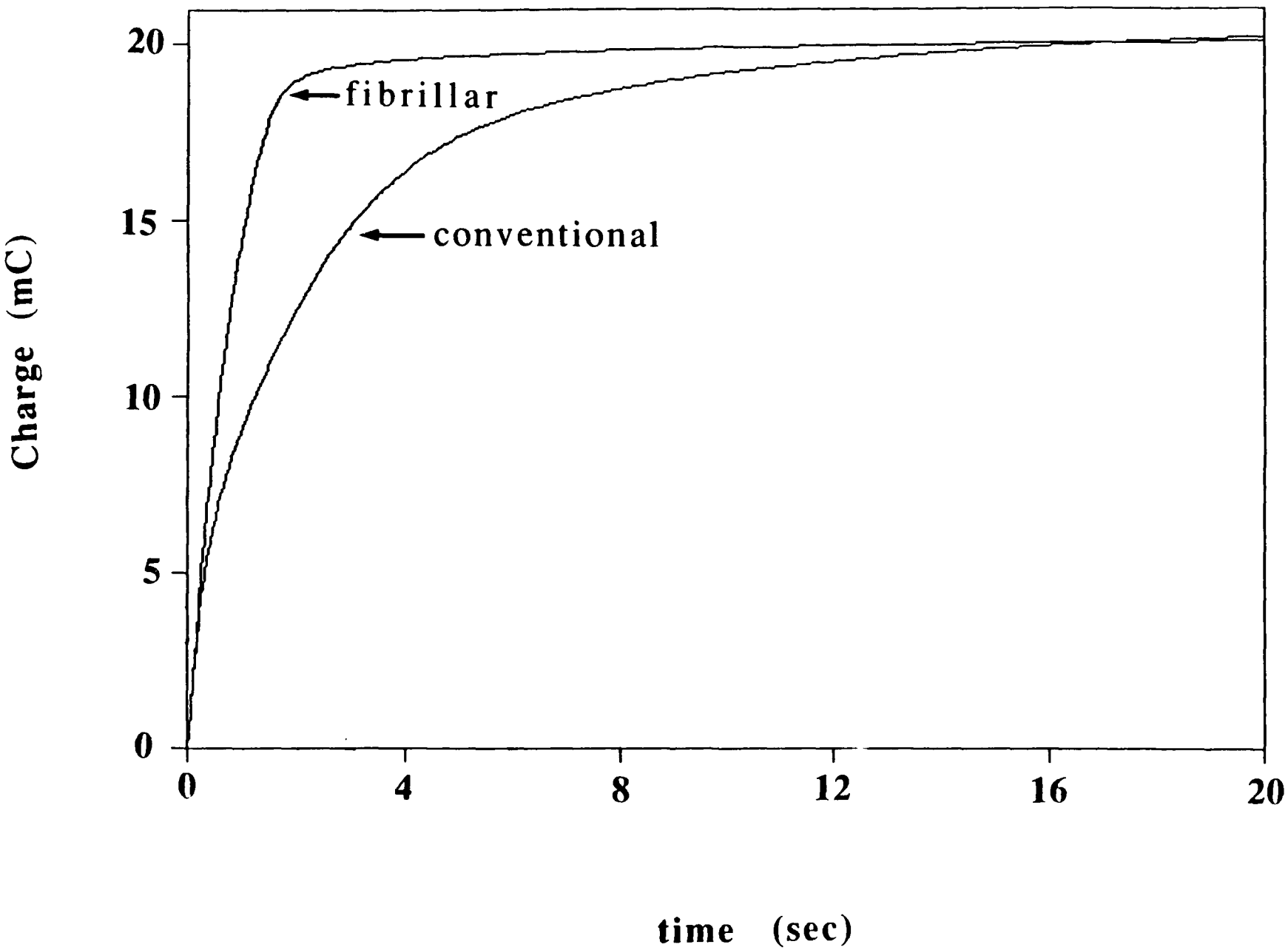
Figure 2 Charge versus time transients for the reduction of a conventional 1.0 μm thick conventional polypyrrole film and a fibrillar polypyrrole film.

Table I. t_{95} values associated with the reduction of various polypyrrole films.

Quantity of Polypyrrole (μmoles pyrrole)	t_{95} (sec)[a]	
	Conventional	Fibrillar
0.44	4.0 ± 1.2	1.7 ± 0.4
0.88	6.5 ± 0.4	2.7 ± 1.6
1.31	7.2 ± 0.8	3.7 ± 0.5
1.75	9.3 ± 0.8	5.9 ± 2.1

[a] Time required to reduce the film to 95 % of maximum charge value.

25KU X15,000 1μm 1010


20
15
10
5
0
Charge (mC)
fibrillar
conventional
0
4
8
12
16
20
time (sec)